2023-sCO2.eu-151

CO_2 PURIFICATION AND PURITY CONTROL FOR THE SCO_2 EXPERIMENTAL LOOP AT REZ – A SUMMARY OF THE TEST RESULTS

Jan Berka*
Centrum výzkumu Řež s.r.o.
University of Chemistry and Technology, Prague
Řež, Prague, Czech Republic
Email: jan.berka@cvrez.cz

Tomáš Hlinčík
University of Chemistry and Technology Prague
Prague, Czech Republic

Eliška Purkarová
University of Chemistry and Technology Prague
Prague, Czech Republic

Alice Vagenknechtová
University of Chemistry and Technology Prague
Prague, Czech Republic

Jakub – Vojtěch Ballek
University of Chemistry and Technology Prague
Prague, Czech Republic

ABSTRACT

In project No. TK02030023, titled 'Purification and purity control of CO_2 gas in power cycles' (funded by the Technology Agency of the Czech Republic [TA CR]), methods for gas purification in an sCO_2 loop were proposed and tested. First, moisture separation was investigated using adsorption techniques, and the initial results of the experiment are presented in this paper.

INTRODUCTION

Power cycles with supercritical carbon dioxide (sCO_2) can be adopted in numerous applications in both nuclear (including advanced Generation IV reactors) and non-nuclear power production. These power cycles are characterised by higher efficiency compared to steam power cycles. Another advantage is the more compact size of their components, particularly the turbine [1, 2]. The operational temperature range of the sCO_2 cycle is wide, typically ca. 350–700 °C.

Various arrangements and configurations of sCO_2 power cycles have been proposed. According to the heat source, the cycles can be designed as 'indirectly fired' or 'directly fired' (see [2] for details). More commonly, indirectly fired cycles use a closed sCO_2 circuit heated by an external heat source over a heat exchanger. Directly fired sCO_2 power cycles use flue gas from combustion as a heat source, as well as CO_2. These cycles can be combined with carbon capture and storage technology [2].

There are various research activities and projects on sCO_2 power cycles, which include investigations into sCO_2 medium chemistry, purification and purity control. Other activities are centred on the compatibility of structural materials with sCO_2 as a medium.

One of these research projects is titled 'Purification and purity control of CO_2 gas in power cycles' (No. TK02030023) and is supported by the Technology Agency of the Czech Republic (TA ČR) [3]. The project has been made possible in cooperation with two organisations, i.e. Centrum výzkumu Řež s.r.o. (CV Řež) and the University of Chemistry and Technology, Prague (UCT). Finalisation of the project is planned for 2025, and its principal objectives are as follows:

- Gain, summarise and utilise information concerning purity, purification processes and analytical purity control techniques for sCO_2 power systems;
- Carry out analytical method verification;
- Implement impurity separation methods, based on adsorption testing;
- Propose and manufacture a purification unit for an sCO_2 experimental loop at CV Řež;
- Propose and manufacture an sCO_2 autoclave for material testing;
- Propose a CO_2 purification system for an sCO_2 power station.

The selected information and specific results obtained during the process of drawing up the project solution are presented in this paper.

ANTICIPATED IMPURITIES IN SCO_2 POWER CYCLES

The first phase of identifying a solution for project No. TK02030023 involved listing the impurities expected in CO_2 and sCO_2 power systems.

Impurities may affect the lifetime, effectivity and reliability of a power station, and sources of impurities can include leakages from the surroundings, desorption from internal surfaces, admixtures in source gas and chemical reactions during operation.

One cause of impurities is the source gas, which is used for filling the system. The purity levels of individual types of CO_2 gases available on the market are different (see the examples in Table 1) [4]. In particular, cheap gases with low purity contain reasonably significant quantities of admixtures.

* corresponding author(s)

DOI: 10.17185/duepublico/77330

Table 1: The CO_2 purity levels of gases available on the market [3] in vppm (1 vppm = 0.0001 % by volume).

CO_2 type	Purity	Impurities (vppm)					
	% vol.	H_2O	O_2	CO	C_nH_m	N_2	Oil
SFC/SFE	99.9993	1	2	0,5	1	3	-
CO2 for food industry (E290)	99.5	52	-	10	-	-	5
4.8	99.998	5	2	1	2	10	-
4.5	99.995	5	15	1	2	30	-
R-744	99.9	10	15	1	2	30	-
3.0	99.9	120	500	-	50	500	-
5.3	99.9993	1	2	0,5	1	3	-

Other impurities seep into the circuit during operation.

In indirectly fired sCO_2 power cycles, during stable operation, only minor impurities are anticipated (in concentrations well below 1 % by volume). The following compounds are likely present in sCO_2: H_2O, O_2, CO, N_2, organic compounds and oil. Some of these compounds may influence the lifetime and reliability of a power station due to corrosion (particularly H_2O). Organic compounds and oil may worsen heat exchange, albeit only in high concentrations.

In the case of directly fired cycles, the concentration of impurities is expected to be higher (in units of % by volume) due to the use of flue gas as a source of CO_2. In this scenario, more compounds, i.e. sulphur oxides, are expected to be present in the sCO_2 power cycle. Other than corroding the power device, these higher impurity levels may also lower the efficiency of the power cycles [3]. Project No. TK02030023 is primarily aimed at the more commonly used indirectly fired sCO_2 power cycles.

In identifying the project solution, the presence of organic impurities in sCO_2 during the experimental loop operation was monitored [3, 4] using gas chromatography and the gas chromatography–mass spectrometry (GC-MS) technique. In the operation of larger (semi-industrial) scale experimental devices, there are fairly common problems with organics in a gas medium for various reasons [5]. Before the operation, the loop was filled with CO_2 with a purity of 4.0; then, the loop was operated at 550 °C and 25 MPa. During operation, several CO_2 extractions were taken through sampling tubes filled with active carbon. Subsequently, the adsorbed organics were determined using GC-MS. The concentration of organic compounds detected was relatively low, with the highest being ca. 1700 ng/l (25 °C, 1 bar) and the concentration decreased during operation (see Figure 1). Of the detected organic compounds, benzene predominated. The source of these organic impurities may have been residual oils and degreasers in the internal apparatus of the sCO_2 experimental loop or oil from the circulator, and sCO_2 is known to be a very effective solvent of organics. Other compounds can also be formed by reactions at a high temperature. The details of the experiment are described in [6].

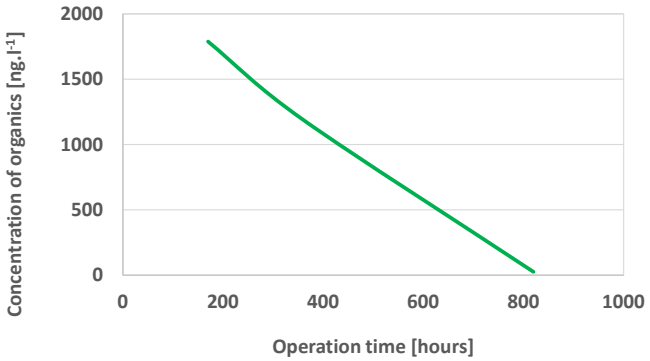


Figure 1: The organic compounds present in sCO_2 during operation of the experimental loop at Řež.

CO_2 ANALYTICAL PURITY CONTROL

To determine the above-mentioned compound concentrations, different methods can be adopted. The applicability of a particular method depends on the required sensitivity, its usability in a specific environment, the demands on operators and purchase costs. General-purpose methods suitable for identifying a wide range of compounds are based on gas chromatography. Therefore, some of the activities carried out in project No. TK02030023 was aimed at researching this technique. The sensitivity and other properties of these methods depend on their configuration and settings (see Table 2 for details).

DOI: 10.17185/duepublico/77330

Table 2: The configurations and basic characteristics of gas chromatography systems.

Configuration	Detector	Utilisation	Sensitivity/detection limit	Note
GC-TCD	Thermal conductivity	Universal	Approx. 10 vppm	Not suitable for mixtures containing H_2 and He as a carrier gas
GC-FID	Flame ionisation	Flammable compounds, sensitive, typically C_xH_y	Not sensitive to permanent compounds	
GC-HID	Helium ionisation	Universal, high sensitivity	Bellow 1 vppm, bellow 0,1 vppm for selected compounds	Requires He as a carrier gas
GC-MS	Mass spectrometry	Universal, depends on the configuration	Suitable, especially for the identification and determination of organic compounds	Demanding in terms of staff qualification, operation conditions, compliance and maintenance. Higher purchase cost.

In addition to the analytical technique, the sampling method is also important. Samples can, for example, be taken in a special vessel (e.g. a sampling canister) or adsorption tube (as in the identification of organics described above) for ex-situ analysis in a laboratory. The sampling site can also be directly connected to the analytical device to reduce the probability of sample contamination by the surrounding air. In the gas sampling of an sCO_2 system (e.g. the experimental loop), the gas pressure must be reduced. The pressure drop is accompanied by a temperature decrease (the Joule–Thomson effect) and freezing of the sampling valve. This phenomenon may affect the results of the analysis due to cold trapping the selected components in the frozen valve (Figure 2). This problem can be resolved using a multistage sampling line and by gradually reducing the pressure with heated reduction valves. For CO_2 sampling in the sCO_2 experimental loop, a three-stage sampling line with a pressure reduction of 12.5→7→2 MPa via heated valves was manufactured (Figure 3).

Figure 2: Freezing the single-valve sampling line during gas sampling.

DOI: 10.17185/duepublico/77330

Figure 3: The three-stage sampling line employing gradual pressure reduction of the sCO_2 in the experimental loop.

To control the analytical purity of the CO_2, the application of gas chromatography with a helium ionisation detector (GC-HID) seemed a suitable configuration because of good sensitivity to most trace-concentration compounds. Thus, this GC-HID chromatographic method was developed, and the standard gas mixture, the composition of which is listed in Table 3, was used to verify the method. The test results are depicted in the form of a chromatogram as shown in Figure 4. The resolution of most of the trace compounds was relatively good; only acetylene is not visible in the chromatogram, establishing the method as suitable for simple gas impurity determination. Nevertheless, for the identification of higher levels of hydrocarbons, either the method would need to be improved or another analytical technique would have to be employed.

Table 3: The model's gas mixture composition.

Compound	Concentration (vppm)
H_2	100
O_2	100
N_2	100
CH_4	500
Acetylene	500
CO	500
CO_2	Bal.

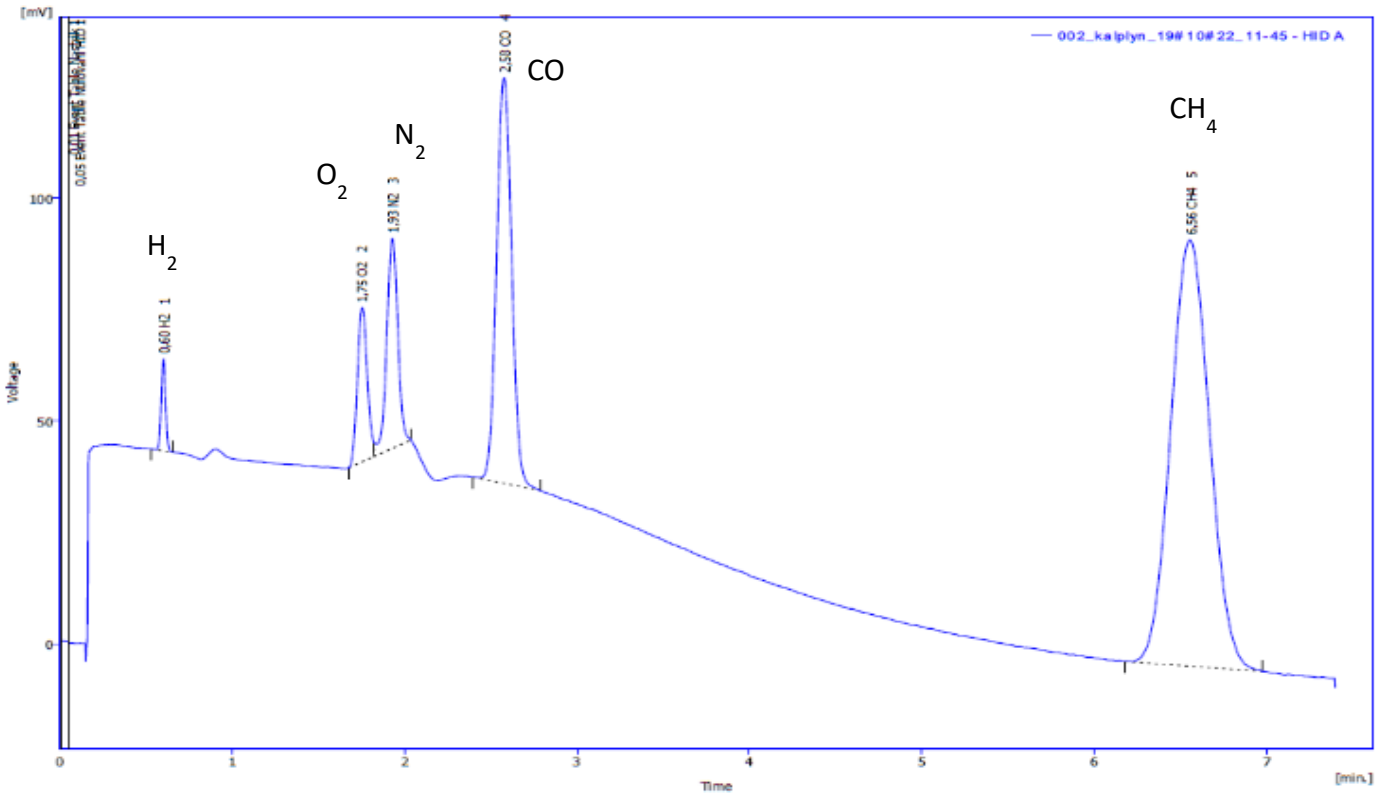


Figure 4: A GC-HID chromatogram of the model gas mixture detailed in Table 3.

DOI: 10.17185/duepublico/77330

Gas chromatography methods are not particularly convenient for detecting and determining moisture (H_2O) content. This is important because moisture typically accelerates corrosion. Special moisture analysers (hygrometers) that operate on different principles are available on the market, and the parameters of some of these are listed in Table 4. Several of these devices enable the probe to be placed directly in the medium, where moisture is monitored. In particular, probes of capacitive and optical hygrometers are designed for higher pressures, which are characteristic of sCO_2 systems.

For the verification of moisture monitoring in the sCO_2 infrastructure at Řež, an infra-red optical analyser was procured. Hygrometers are also used in the natural gas industry; according to the German manufacturer, standard probes are designed for 10 MPa and special probes (recommended for sCO_2 systems) are designed for a pressure of 20 MPa and tested at 25 MPa. The system can further be calibrated for use in a CO_2 environment. However, the manufacturer states that the measurement accuracy cannot be guaranteed under supercritical conditions and that, to achieve an accurate measurement, the recommended conditions for the probe site are a pressure range of 0.1–5 MPa, a temperature range of 10–40 °C and the maintenance of stable values. To create these conditions, both the pressure and temperature of the probe site must be reduced. The system will be tested during the next experimental phase of this project.

Table 4: Selected methods for moisture determination

Method	Max. pressure (MPa)	Measurement range (dew point °C)	Uncertainty (°C)	Note
Cooled mirror	1,1 (2)	- 35 až + 25 (- 65 až + 25)[a]	± 0.2	[a]Depends on the connected probe
Cooled mirror (mobile)	10	- 35 až + 25 (-50 až + 25)[b]	± 1	[b]Depends on the ambient temperature
Optical	25	- 80 až + 20	± 1	
Capacity	34.5	- 80 až +10	± 2 (± 3)	Frequent calibration is needed to maintain measurement accuracy
Quartz crystal microbalance – QCM	0.4	- 80 až - 13	± 3 až ± 1	
Tuneable diode laser absorption spectroscopy – TDLAS	0.17	- 71 až - 2,6*	± 4 až ± 0,1	

.

PROPOSAL FOR AND VERIFICATION OF A CO2 PURIFICATION SYSTEM

The proposed purification unit for the sCO_2 experimental loop in Řež should predominantly extract H_2O and, if possible, other impurities in the form of residual organic compounds, such as CO, H_2 and O_2 from the CO_2 in the loop. The unit is based on the principles of oxidation and adsorption. The proposed purification unit will be set up and implemented in the next phase of the project.

In this phase, the moisture separation was tested with a laboratory device at UCT in Prague (see Figure 5). The gas was saturated to the requisite moisture level using a moisture generator (1) and subsequently passed through the adsorber (2), where the adsorbents were tested. The moisture level of the outlet gas was measured by way of three hygrometers operating on different principles: cooled mirror, capacity and infra-red.

The moisture separation was tested on three selected adsorbents, i.e. silica gel, a 13 X molecular sieve and active carbon SC 40 (Figure 6). The tests were performed with CO_2 and nitrogen to simulate the effects of a gas matrix.

The results are shown in the graphs in Figure 7 and can be summarised as follows:

DOI: 10.17185/duepublico/77330

- For higher levels of moisture adsorption, both the silica gel and 13 X molecular sieve were effective.
- When the moisture concentration in the inlet gas was low, the 13 X molecular sieve was more effective.
- Active carbon AC 40 was not found to be suitable at all for moisture adsorption.
- The adsorption capacities of the nitrogen matrix gas were approximately 20 % higher than those of the CO_2 matrix gas, with CO taking up part of the adsorbent capacity.

In accordance with the results, the 13 X molecular sieve is recommended as a filler in the purification unit for the experimental loop.

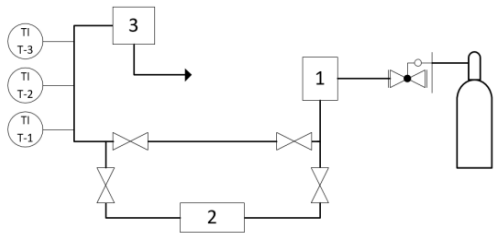
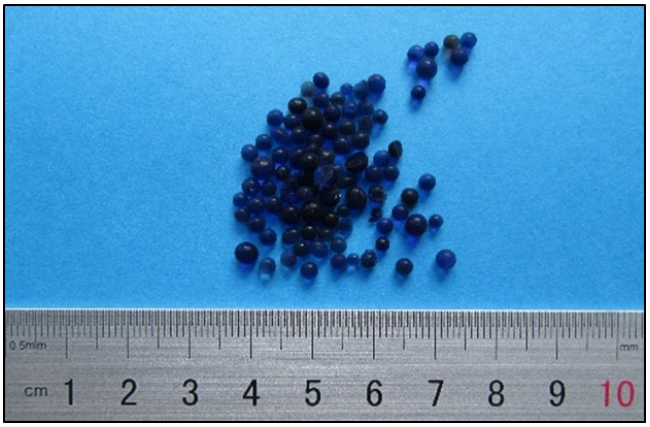


Figure 5: The laboratory device for moisture separation testing. 1 – moisture generator; 2 – adsorber; 3 – gas meter; T-1 – Moisture Monitor Series 35; T-2 – hygrometer HYGROPHIL Model F 5672; T-3 – cooled mirror hygrometer HYGRO M4.



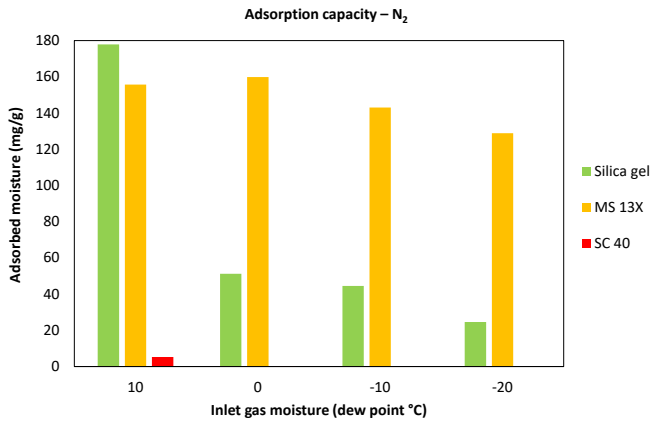
a)

b)

c)

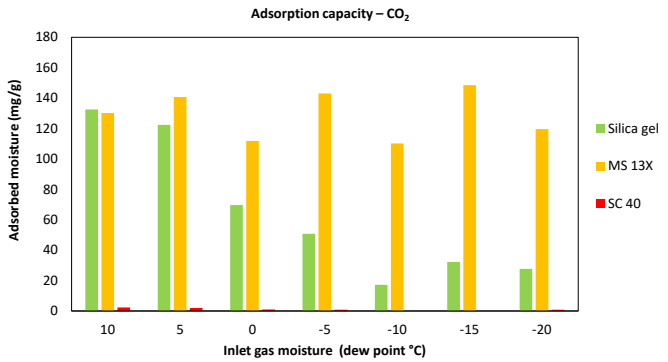
Figure 6: The tested adsorbents for moisture removal: a) silica gel; b) 13 X molecular sieve; c) active carbon SC 40.

The experimental programme is still being conducted, and the removal of other selected impurities is planned for the next phase. Verification of the adsorbents' resistivity in a CO_2 environment in a special sCO_2 autoclave is also planned. The autoclave is currently under construction.



a)

DOI: 10.17185/duepublico/77330



b)

Figure 7: Results of the moisture adsorption tests: a) with a nitrogen gas matrix; b) with a CO_2 gas matrix.

CONCLUSION

CV Řež. and the Department of Gaseous and Solid Fuels and Air Protection, UCT participated in the research activities described herein concerning the purification and purity control of CO_2 in sCO_2 power cycles. In these activities, methods for CO_2 purification and purity control were proposed and verified. Gas chromatography with a helium ionisation detector and an optical infrared hygrometer appeared to be the most effective combination for removing the majority of impurities that were expected to be present in sCO_2 monitoring. These methods were sufficiently sensitive for concentrations of compounds from 0.1–1 vppm. The application of gradual pressure reduction via heated valves in a sampling line prevented it from freezing. The tests of impurity extraction from the CO_2 gas are currently in progress; in the first instance, the adsorption of moisture by different types of materials is currently being investigated. According to the experimental results obtained, the 13 X molecular sieve seemed to be effective for H_2O adsorption from gas with both higher and lower moisture concentrations. The research activities will continue for at least several more years, and another set of results is expected.

ACKNOWLEDGEMENTS

The presented work was funded by TA CR, project No. TK02030023.

REFERENCES

[1] SCO2 Power Cycles for Fossil Fuels. Department of Energy. [online]. [vid. 2020-04-03]. Available at: https://www.energy.gov/sco2-power-cycles/sco2-power-cycles-fossil-fuels.

[2] Brun, K., Friedman, K., Dennis, R. (2017). Fundamentals and Applications of Supercritical Carbon Dioxide (sCO2) Based Power Cycles. Duxford, United Kingdom: Elsevier. 465 s. ISBN: 978-0-08-100804-1

[3] Available at: https://backup.isvavai.cz/cep?s=jednoduche-vyhledavani&ss=detail&n=0&h=TK02030023

[4] Berka, J., Hlinčík, T., Purkarová, E., Vagenknechtová, A., Rozumová, L. Investigation of material degradation and coolant chemistry for sCO2 power cycles. The 4th European sCO2 Conference for Energy Systems March 22–26, 2021, Prague, Czech Republic, paper No. 139

[5] Berka, J., Víden, I., Kozmík, V. (2012): Organic Compounds Detectable in the He Loop of Experimental Research Device for Simulation of Nuclear Reactor Cooling at Opening Operation, Chem. Listy 106, 980-987

[6] Berka, J., Ballek, J. V., Velebil, L. et al. (2021): CO_2 power chemistry in the CV Řež experimental loop, Acta Polytechnica, vol. 61, no. 4, p. 1-7, doi: 10.14311/AP.2021.61.0504

DOI: 10.17185/duepublico/77330

DOI: 10.17185/duepublico/77330
URN: urn:nbn:de:hbz:465-20230427-151319-7